Simulation of dopant atom behavior in semiconducting nanocrystals

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Introduction

In modern electronics, dopant atoms are essential to the performance of nearly all semiconducting devices. Atomic-scale knowledge of dopant location becomes essential on the nanometer scale when only a handful of dopants exist within a crystal. The location of these impurities, whether taking an existing atom's spot or squeezing into an interstitial site, can significantly alter the optoelectronic properties of the material. Currently, HAADF-STEM allows for direct 3-D location of dopant atoms whose atomic number is significantly larger than the host lattice; however, dopant atoms whose atomic number is similar to the host lattice (and more realistic for current applications) is a more challenging problem that requires careful quantitative analysis of both HAADF-STEM images and EELS spectra [1]. To access this information, it is important to simulate imaging conditions. This work centers around preparing scripts that fluidly generate a variety of user-specified doped nanocrystals for multislice simulation of HAADF-STEM images for dopant visibility analysis and comparison to experimental results.

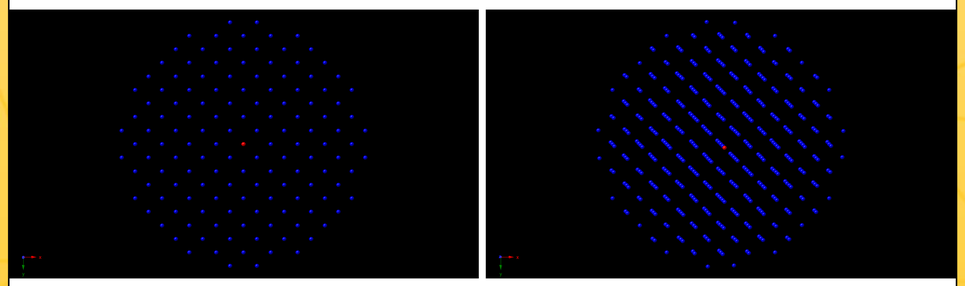
Generation of nanocrystals

Script Features

- Generate output files for both CrystalMaker and Kirkland's computem
- Capable of producing multiple crystal structures
- User-specified particle diameter
- Insert any number of substitutional and/or interstitial dopant atoms, when allowed by the structure
- User-specified zone axis

How it works

- Expand unit cell coordinate matrix into lattice through repeated concatenation; delete repeated atom positions
- Remove all atoms outside of the desired particle radius to create a sphere
- Take user-specified dopant atoms and fit them to the closest allowed substitutional or interstitial site using a minimum distance method
- Apply rotation matrices to spherical lattice to achieve desired zone axis and tilt
- Write number of atoms and their coordinates to CrystalMaker output file



- 2.5 nm Arsenic-doped silicon nanocrystal viewed along the [001] zone axis in CrystalMaker. Crystal shown at zero tilt (left) and two degrees in the x and y directions (right). The arsenic atom is shown in red.

Simulations – basics

- Multislice simulations generate images based on parameters set in real TEM experiments. The input contains the identity and location of every atom in the crystal, their fractional occupancy and phonon amplitude, and the detector geometry [2].

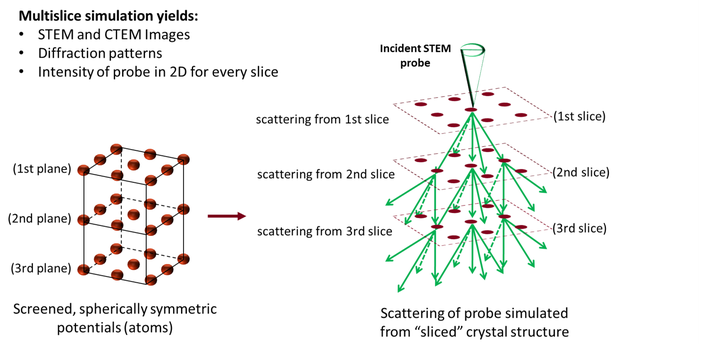
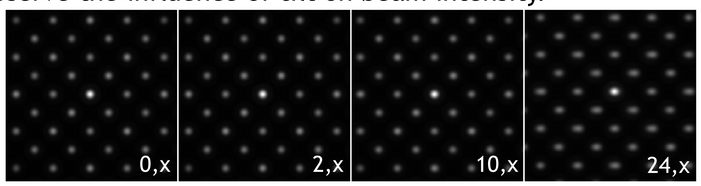


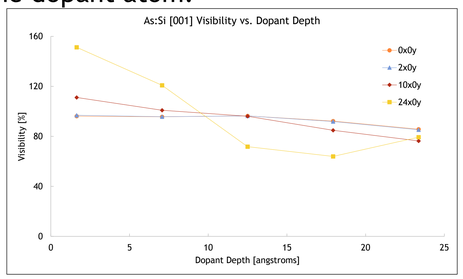
Figure credit Michael Odlyzko

Effect of tilt on visibility

In this study we aim to evaluate the effect of slight mistilts of experimental HAADF-STEM analysis on doped nanocrystals, which has been largely ignored by previous analyses. [001] Si was doped with As in the central column of atoms at different depths and was tilted in the x and y directions to observe the influence of tilt on beam intensity.



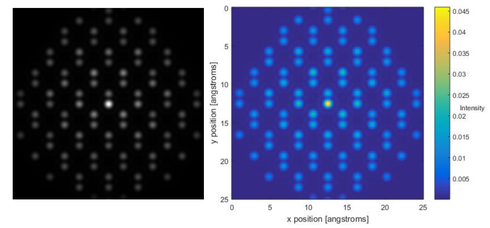
- Crystal tilt is in the magnitude (in mrad) and direction specified in the images. The As atom lies in the center of the sphere.
- $visibility = 100\% \times \frac{I_{dopant} - I_{intrinsic}}{I_{intrinsic}}$ where *I* is the summed intensity of a given spectrum over a 5x5 pixels region around the dopant atom.



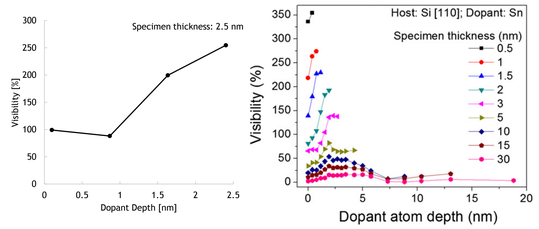
- Preliminary investigation shows that significant changes in visibility occur at these slight mistilts, contrary to expectation.

Effect of dopant depth on visibility

[110] silicon was doped with tin at different depths along the center column of atoms; effect on beam intensity was observed.



- Simulated images at zero tilt. STEM image (left) shows the x-y location of the tin atom as a bright spot; the intensity color map (right) shows the dopant as a yellow spot.



- Visibility as a function of dopant atom depth in Sn-doped Si. My simulations without the inclusion of phonon scattering (left) follow the same trend as those by Mittal et al. [3] with phonon scattering (right). The inclusion of phonons decreases contrast.
- Significant increases in visibility are observed after the dopant is approximately halfway down the column.

Conclusions

- My script creates nanocrystals ideal for TEM simulations, where dopants and tilt can be arbitrarily specified and the zone axis fluidly changed.
- Changes in visibility (as a function of depth) in [001] As-doped Si are unexpectedly large at slight mistilts and require further experimentation.
- [110] Sn-doped Si exhibits a significant increase in visibility after the dopant becomes located at least halfway down the z-direction of the crystal. The inclusion of phonon scattering should put the two methods in nearly perfect agreement.

References & Acknowledgement

[1] A. A. Gunawan et al. *Nano Lett.*, (2011) 11, 5553-5557
[2] E. J. Kirkland, *Advanced Computing in Electron Microscopy*, 2nd Ed., Springer (2010)
[3] A. Mittal et al. *Ultramicroscopy*, 111 (2011) 1101-1110

Key Terms
HAADF-STEM: high-angle annular dark-field scanning transmission electron microscopy
EELS: electron energy loss spectroscopy

I would like to acknowledge both the Undergraduate Research Opportunities Program and the Mkhoyan Group in the completion and submission of this work.